EPA-600/R-04/167
December 2006

Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls Modeling Report

Prepared for

U.S. Environmental Protection Agency
Great Lakes National Program Office
77 West Jackson Boulevard
Chicago, Illinois 60604

Prepared by

U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Mid-Continent Ecology Division
Large Lakes and Rivers Forecasting Research Branch
Large Lakes Research Station
9311 Groh Road
Grosse Ile, Michigan 48138

Ronald Rossmann, Editor

Printed on Recycled Paper

Notice

The information in this document has been obtained primarily through funding by the United States Environmental Protection Agency (USEPA) under the auspices of the Office of Research and Development (ORD) and by the Great Lakes National Program Office (GLNPO). The report has been subjected to the Agency's peer and administrative review and it has been approved for publication as a USEPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Foreword

The Lake Michigan Mass Balance Project (LMMBP) was initiated by the United States Environmental Protection Agency (USEPA), Great Lakes National Program Office (GLNPO) to determine strategies for managing and remediating toxic chemicals in the lake basin. Within the ecosystem approach, the mass balance framework is considered the best means of accomplishing this objective, and GLNPO requested the assistance of the USEPA Office of Research and Development (ORD) to facilitate and produce mathematical models that account for the sources, sinks, transport, fate, and food chain bioaccumulation of certain chemicals. This approach has been used in the past and builds upon the modeling efforts that have occurred in the Assessment and Remediation of Contaminated Sediments (ARCS) Program and the lower Fox River/Green Bay Mass Balance Project. The feasibility of such studies and resultant alternative management options for contaminants in large rivers and a large embayment were demonstrated, and a logical extension to the entire Lake Michigan receiving water body and major tributaries was warranted. There were a large number of cooperators in this project, and by focusing Federal, State, local, private, and academic efforts and resources on a common goal, much more was accomplished than if these entities acted independently.

The project was conducted in conjunction with the Enhanced Monitoring Program and the approach required that all monitoring and field research be coordinated and common methodologies used. Mathematical modelers were consulted during planning for sample design, parameters, and temporal and spatial sampling considerations. The product was then a consistent and reliable database of information that was accessible by project participants and the public. Data for the LMMBP were collected primarily during 1994 and 1995 and have been compiled according to specified quality assurance/quality control (QA/QC) requirements, and other data assessments have been made for modeling purposes.

The need to consider the environmental benefits and consequences of alternative remediation choices to protect and improve our environment continues to intensify as: 1) environmental problems become more complex; 2) the means to address and investigate problems become more technical, time-consuming, and expensive; and 3) the actual costs to implement action strategies has escalated. The integrated PCBs mass balance modeling results are presented in this document and can aid managers in establishing priorities for both lake-wide and local improvements. The forecasting of PCB concentrations in top predator fish is one of the primary endpoints of this investigation as it relates to both ecosystem and human health. The capability of forecast modeling presented here is a salient feature of this approach directed toward providing multiple alternatives, which then can be examined through benefit-cost analyses.

This report presents the current status and results of the PCB modeling effort through the summer of 2006. Within this document some recommendations have been provided for potential future work with the models. Of course, a model and modeling applications are never complete, and it is expected that further efforts will change some results, insights, and our understanding of Lake Michigan. These efforts require an investment of resources and time, and improvements with additional model run executions are measured in years. In the larger picture, the need for Agency modeling technologies continues to intensify and the requirement for reduced uncertainty will lead to future improved generations of models. We have put great emphasis on following guidance provided by the USEPA and other agencies in assuring that the scientific theory is implemented accurately and completely by model computer code and that best modeling practices have been instituted. We also submitted this to scientific peer review using an interdisciplinary panel of scientists and experts that reviewed model theory and application which evolve on a continuing basis. The purpose is to ensure that decisions based on the modeling efforts are reliable and scientifically credible.

This document is not intended to include all of the details and background required to understand the entire LMMBP. Rather the reader should refer to the LMMBP Work Plan and other materials on the GLNPO web site and the Lake Michigan Mass Balance Modeling Quality Assurance Plan on the ORD-Grosse Ile web site for further information.

This document includes replies to peer reviewer comments made during a peer review conducted 27-28 July 2004 in Romulus, Michigan. These replies and the original peer review comments are found in Part 7.

Abstract

The Lake Michigan Mass Balance Project (LMMBP) was conducted to measure and model nutrients, atrazine, polychlorinated biphenyls (PCBs), *trans*-nonachlor, and mercury to gain a better understanding of the sources, sinks, transport, fate, and effects of these substances within the system and to aid managers in the environmental decision-making process for the Lake Michigan Basin. The United States Environmental Protection Agency (USEPA) Office of Research and Development (ORD) was requested to conduct and facilitate modeling in cooperation with the USEPA Region V; the USEPA Great Lakes National Program Office (GLNPO); other Federal agencies; the States of Michigan, Wisconsin, Illinois, and Indiana; the Tribes; and the public and private sectors. The effort was supported by intensive sampling of the atmosphere, major tributaries, sediments, water column, and biota during the 1994-1995 field years as well as by extensive quality assurance and database development. Multimedia, mass balance modeling frameworks were applied to examine primary source and loss categories and make various model forecasts for a variety of loading scenarios. This report focuses on the modeling practices applied and results for PCBs from the MICHTOX screening-level model and the higher-resolution LM2-Toxic and LM Food Chain models. A unique aspect of this work is the modeling of PCBs on a congener-level basis to make predictions of total PCBs in the system.

Results of the system mass balance show that the greatest, external gross input of PCBs to the system is atmospheric vapor phase absorption followed by tributary inputs and atmospheric deposition, respectively. The greatest gross losses from the system are volatilization and deep burial in sediments. Internal PCBs loading from sediment resuspension is substantial. Gross PCBs inputs to, losses from, and cycling processes within the system each typically exceed 1000 kg/year. Tributary inputs and atmospheric deposition are approximately 381 and 980 kg/year, respectively. Results indicate that during the mass balance field collection years of 1994-1995, the Fox, Grand, Calumet, and Kalamazoo Rivers had the largest tributary loads of PCBs to Lake Michigan. When all gross input and output fluxes are summed, the system exhibits a net loss of approximately 3,229 kg/year of PCBs. The mass balance results demonstrate the importance of contaminant cycling and the dynamic interactions among air, water, and sediments. These interactions, with present PCB inventories already in the lake, will continue to control PCB concentrations in the system.

LM Food Chain, linked to LM2-Toxic, and MICHTOX were used to forecast future concentrations of PCBs in lake trout at two sites for various loading scenarios. Scenarios included constant 1994-1995 conditions, fast continued recovery with an atmospheric load half-life of 6.0 years, slow continued recovery with an atmospheric load half-life of 20.0 years, and various combinations of reduced atmospheric and tributary loadings. Forecasts indicate that PCBs concentrations in lake trout will continue to decrease. For the fast continued recovery scenario, the target level for the unrestricted consumption of fish (0.075 ppm) was forecasted to be achieved for five to six year-old lake trout between the years 2030 and 2036. The narrow forecast range for scenarios, past actions, the long-term decrease in loads, and decreasing PCB concentrations in the system indicate that PCBs are presently controlled by dynamic interactions among media, as well as air and sediment cycling. Model results from the present two models are compared. In the future, these results will be compared to those from a greater-resolution model under development (LM3-

Toxic). It is anticipated that the higher-resolution model will better delineate the nearshore and sediment zones, define lake interactions with tributary inputs, and describe PCBs in lake trout populations.

This synthetic lake-wide perspective is anticipated to aid managers in moving forward on pollution prevention, remedial actions, and legislative priorities associated with the Lake Michigan Lake-wide Management Plans. It will also help describe expected local improvements associated with Remedial Action Plans in Areas of Concern. *This abstract does not necessarily reflect USEPA policy*.

Table of Contents

List of Figures

List of Tables

Abbreviations

AOCs	Areas of Concern
AREAL	Atmospheric Research and Exposure Assessment Laboratory
BIC	Biotic carbon
BMC	Bayesian Monte Carlo
BNL	Benthic nepheloid layer
CCC	Criterion continuous concentration
CMC	Criterion maximum concentration
CPE	Catch per unit of effort
CTF	Contaminant transport and fate model
DDE	Dichlorodiphenyldichloroethylene
DEA	Deethylatrazine
DIA	Deisopropylatrazine
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphorus
DQO	Data quality objectives
DSi	Dissolved silica
EEGLE	Episodic Events-Great Lakes Experiments
EMP	Enhanced Monitoring Program
GLERL	Great Lakes Environmental Research Laboratory
GLNPO	Great Lakes National Program Office
GLWQA	Great Lakes Water Quality Agreement
GBMBP	Green Bay Mass Balance Project
HOC	Hydrophobic organic chemicals
IADN	Integrated Atmospheric Deposition Network
IDL	Instrument detection limit
IDW	Inverse distance weighted
LaMP	Lake-wide Management Plan
LLRFRB	Lake Lakes and Rivers Forecasting Research Branch
LLRS	Large Lakes Research Station
LMMBP	Lake Michigan Mass Balance Project
LOC	Labile organic carbon
LON	Labile organic nitrogen
LOP	Labile organic phosphorus
MCL	Maximum contaminant level
MDEQ	Michigan Department of Environmental Quality

MDL	Method detection limit
MED	Mid-Continent Ecology Division
MQO	Measurement quality objectives
NHEERL	National Health and Environmental Effects Research Laboratory
NOAA	National Oceanic and Atmospheric Administration
ORD	Office of Research and Development
PCBs	Polychlorinated biphenyls
PDC	Particulate detrital carbon
PI	Principal Investigator
POC	Particulate organic carbon
POM	Princeton Ocean Model
POP	Persistent organic pollutants
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
RAPs	Remedial Action Plans
RDMQ	Research Data Management and Quality Control System
RFS	Routine field sample
ROC	Refractory organic carbon
RON	Refractory organic nitrogen
ROP	Refractory organic phosphorus
SA	Available silica
SDA	Specific dynamic action
SDL	System detection limit
SRP	Soluble reactive phosphorus
SU	Biogenic silica
TKN	Total Kjeldahl nitrogen
TMDL	Total maximum daily load
USDOI	United States Department of Interior
USEPA	United States Environmental Protection Agency
USFWS	Unites States Fish and Wildlife Service
USGS	United States Geological Survey
VWA	Volume-weighted average

Acknowledgments

Special thanks to the United States Environmental Protection Agency, Great Lakes National Program Office for leadership, support, and collaboration on the Lake Michigan Mass Balance Project. The multiple efforts by the Principal Investigators for providing data, necessary for the modeling, are greatly appreciated. Thank you to David H. Miller, Kenneth R. Rygwelski, Timothy J. Feist, Xiaomi Zhang, and James P. Pauer for providing internal technical reviews of various parts of this document. Thanks to Kay Morrison for the graphic renditions and figures and to Debra L. Caudill for formatting and word processing. Finally, thanks to Robert B. Ambrose, Jr., Joel E. Baker, Ken G. Drouillard, Barry Lesht, and James L. Martin for serving on the peer review panel.

Executive Summary

The Lake Michigan Mass Balance Project (LMMBP) provided an opportunity to improve the quality of polychlorinated biphenyl (PCB) mass balance models used to represent large, freshwater ecosystems. A rigorously quality-assured large supporting data set derived from samples collected during eight cruises in 1994-1995 was used to establish atmospheric and tributary loads, estimate initial conditions, perform model calibration and confirmation and, to a lesser extent, to assist in estimating a number of kinetic coefficients. A significant aspect of this modeling effort was modeling PCBs at a congener-level basis.

Lake Michigan is acted upon by a number of physical parameters that impact the hydrology, chemistry, and biology of the lake. For a lake the size of Lake Michigan, changes in these parameters can lead to significant changes, especially when models are used in long-term predictions to predict the outcome of various scenarios. The primary driving forces are wind, air temperature, and precipitation. These impact tributary flows, lake levels, waves, water circulation, water temperature, and ice cover. For the period of record, these driving forces vary from year-to-year. The period of 1982 to 1983 was used to calibrate the hydrodynamic models. For this period of time, hydrodynamic conditions were not at any extreme. This is also true for the period of 1994 and 1995 when the models were applied.

Major physical forcing functions were not extreme during the sampling period of 1994-1995 or the hydrodynamic model calibration period of 1982-1983. Precipitation was within the normal range for all years of modeling interest, resulting in lake levels and tributary flows that were within normal bounds.

Temperature will impact the eutrophication and contaminant modeling. Air temperature impacts how quickly the lake warms in any one year. Water temperature is critical to the timing of algae blooms, especially the spring diatom bloom. It also impacts the volatilization of contaminants. There appears to be a four-year cycle of quicker warming which exists within a trend of general warming of the lake. The trend of warming may be part of a longer term, undocumented cycle, or may be related to climate change.

Models developed at the United States Environmental Protection Agency's Large Lakes Research Station, including LM3-Eutro, MICHTOX, LM2-Toxic, and LM Food Chain, utilized results from a hydrodynamic model to describe the lake's physics and results from air and tributary models to provide loadings to the lake.

LM3-Eutro uses state-of-the-science eutrophication kinetics to simulate the interactions between plankton and nutrients. LM3-Eutro is a high-resolution (44,042 cells and 19 sigma layers) carbon based model that provides a highly resolved description of areas such as near and off shore zones, bays, river confluences, and the thermocline. Its nutrient variables include dissolved, labile particulate, and refractory particulate forms which provide a more realistic description of phytoplankton-nutrient interactions. Improvements were made to the light calculation by using a three-hour rather than 24-hour (one day) average estimate of solar radiation. The model is driven by the Princeton Ocean hydrodynamics Model which simulates water movements. LM3-Eutro has 17 state variables, including a single zooplankton class, two phytoplankton classes, and several particulate and dissolved nutrient (including carbon) states.

The model was calibrated on the high-resolution (44,042 cells) Level 3 framework as well as the 41 segment Level 2 framework. The Level 2 calibration enabled us to visually observe known spatial and temporal trends such as the spring diatom bloom and phytoplankton concentration gradients between the epilimnion and hypolimnion. The Level 3 calibration was performed on a whole-lake basis. The 1994-1995 LMMBP field data were used to calibrate the model. The final calibration was chosen based on the best Level 3 calibration, but Level 2 output was visually inspected to ensure that expected phytoplankton and nutrients trends were reflected. Model confirmation was performed by comparing the model to limited total phosphorus data for 1998 and 2000 and to a historical model, MICH1, which was developed and calibrated in the 1970s and modified more recently. All comparisons were done on a whole-lake basis, and LM3-Eutro fits the 1998 and 2000 data well. LM3-Eutro and MICH1 compared surprisingly well, especially given the fact that they are based on very different frameworks, kinetics, and segmentation. Compared to field data and LM3-Eutro predicted, MICH1 underpredicted both total phosphorus concentrations. This was probably due to the fact that MICH1 does not have any phosphorus sediment recycling. Lower phosphorus values also cause MICH1 to under-predict chlorophyll *a* concentrations in the lake.

MICHTOX is a toxic chemical mass balance and food chain bioaccumulation model developed in the early 1990s. A Bayesian Monte Carlo uncertainty analysis demonstrated that MICHTOX predicted PCB concentrations should be within a factor of two measured data. During the early part of the LMMBP, MICHTOX was updated and used as a preliminary assessment tool of the LMMBP PCB data and to provide a screening-level analysis of the potential future trends in total PCB concentrations in Lake Michigan water, sediment, and fish under a variety of contaminant load scenarios. Unmonitored tributary inputs were added to the model and the applicability of MICHTOX for predicting Lake Michigan total PCB concentrations in water, sediment, and fish was reconfirmed. MICHTOX was applied using the previously developed parameterization and LMMBP data and forcing functions. The model fit to data was acceptable with no adjustments to the model parameters. The model also provided a comparison of an older, "off-the-shelf" model with the more complex models developed as part of the Lake Michigan Mass Balance Project (LMMBP). MICHTOX was run for seven scenarios to help evaluate the impacts on PCB trends caused by various loading sources and to evaluate loading scenarios. Results of the MICHTOX modeling indicate that atmospheric exchange is a dominant loss process of total PCBs in Lake Michigan, and that the reservoir of total PCBs in the sediment has a significant impact on the future trends in concentrations of total PCBs in lake trout.

LM2-Toxic is a sophisticated and state-of-the-art toxic chemical fate and transport model for Lake Michigan. It is a coupled mass balance of organic carbon solids and toxic chemical (PCBs) dynamics. Using the LMMBP generated field data, the organic carbon solids dynamics were first calibrated. This was followed by the independent calibration of PCB dynamics. The temporal variations of both biotic carbon (BIC) and particulate detrital carbon (PDC) resulted from an algal bloom in late spring and early summer. Primary production was the dominant organic carbon load to Lake Michigan. The eutrophication model (LM3-Eutro) generated primary production accounted for over 90 percent of the total particulate organic carbon load to the lake.

The main focus of this model is to address the relationship between sources of toxic chemicals and their concentrations in water and sediments of Lake Michigan and to provide the PCB exposure concentrations to the bioaccumulation model (LM2 Food Chain) to predict PCBs concentrations in lake trout tissue. LM2-Toxic is a revision of the USEPA supported WASP4 water quality modeling framework. It incorporates the organic carbon dynamics featured in GBTOX and the sediment transport scheme, a quasi-Lagrangian framework, used in the IPX. Both GBTOX and IPX were WASP4-type models and major components in the Green Bay Mass Balance Study modeling framework. Another important modification was the addition of updated air-water exchange formulations to the model.

The results at 5 x 5 km^2 grid generated by Princeton Ocean Model for the Great Lakes (POMGL) were linked to the transport fields for LM2-Toxic. Due to an affinity of PCBs for organic carbon, three organic carbon sorbents were simulated as state variables in LM2-Toxic. They were BIC, PDC and dissolved organic carbon (DOC). The model simulated 54 PCB congeners which accounted for 63% to 85% of the total PCB mass in various media for Lake Michigan. This was an enormous effort because individual congeners or co-eluting congeners were modeled as separate state variables in the mass balance, each with their own physical/chemical properties. Four phases were simulated in LM2-Toxic for the congeners. The four phases were dissolved, sorbed to PDC, sorbed to BIC, and bound to DOC.

To reduce uncertainties associated with water transport, settling and resuspension, and sedimentation, a thermal balance model, a chloride model, a long-term simulation using a ^{137}Cs and $^{239,240}Pu$ model, and a long-term organic carbon simulation using LM2-Toxic were developed and run for LM2-Toxic confirmation.

Air-water exchange of PCBs was the most important process for Lake Michigan. Net sediment resuspension was the second largest net source. Both the water column and the surficial sediment layer of the lake were not at steady-state during the LMMBP period. The model was also applied for forecasting the long-term responses (60-year simulation, starting on January 1, 1996) of the PCBs in Lake Michigan under various forcing functions and load reduction scenarios. The results indicate that the PCB mass in the surficial sediment is large and thus could support PCB concentrations in the water column for a very long time.

LM Food Chain is the food web bioaccumulation model developed for the LMMBP. The model established dynamic relationships between PCBs concentrations in the exposure environments and resulting PCBs levels in the lake trout food webs of Lake Michigan. The model was based upon available theory and data characterizing the bioaccumulation of toxic chemicals in fish and other aquatic organisms. Samples collected for the LMMBP were used to generate data on lake trout and coho salmon food webs in Lake Michigan and to facilitate refinement of model parameters to site-specific conditions for forty PCB congeners or co-eluters that represented toxic chemicals covering a wide range of hydrophobicity.

The food web model was calibrated with PCB data collected in 1994 and 1995 for lake trout food webs at Sturgeon Bay, Sheboygan Reef, and Saugatuck. The lake trout sub-populations in these three biota zones were believed to be appropriate representations of lake trout in Lake Michigan. Model calibration was also performed for a lake-wide coho salmon food web. During the model calibration, model parameters were refined to achieve an adequate agreement between model calculations and observed PCB data for a food web. The focus of model calibration was not limited to top predators or to toxics with a certain hydrophobicity. The model parameters were systematically optimized for all species at various trophic levels and for PCB congeners of a wide range of hydrophobicity. Extra care was taken to ensure the refined parameter values were consistent with the hydrophobicity of individual PCB congeners and with the trophic position of individual species. Satisfactory calibration results were achieved for the lake trout food webs at Sturgeon Bay and Saugatuck. The model parameters calibrated with data from the Sturgeon Bay food webs were independently tested and validated with data from the Saugatuck food web, and *vice versa*.

The availability of a complete account of observed data for each food web made this model calibration probably the most thorough process among similar efforts. Although PCB concentrations in lake trout or coho salmon were the endpoint of the model computation and the focus of most model applications, the food web model with parameters "fine-tuned" for species at all trophic levels can be used to target any desirable species in the food web with a high degree of confidence. Also, the food web model can be used to model toxics with various hydrophobicities. No food web model intended to simulate as many toxic chemicals with diverse hydrophobicity has been previously developed.

The validated food web model was applied to the lake trout food webs at Sturgeon Bay and Saugatuck and inferred for the southeastern and northwestern regions of the lake to predict future PCB concentrations. Several model simulations were performed to predict the expected changes in future lake trout PCB concentrations in response to different exposure scenarios. Hypothetical long-term PCB exposure scenarios in the post-1994/1995 period for the food webs at the Sturgeon Bay and Saugatuck biota zones were generated by the water quality model LM2-Toxic. For each lake trout food web, the resulting concentrations of individual PCB congeners in fish were predicted. Similar model predictions were observed for these two biota zones under each reduction scenario. For the continued fast recovery scenario, current simulations indicate that the total PCB concentrations in adult lake trout (5.5 years old) were expected to reach the target level of 0.075 ppm in 2030 for the Saugatuck biota zone, 2033 for southeastern Lake Michigan, 2036 for northwestern Lake Michigan, and 2036 for the Sturgeon Bay biota zone.